

# $\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ : a new $\text{V}^{4+}$ layer structure related to $\text{VOF}_3$

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## Abstract

The title compound,  $\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ , (I), features a new infinite,  $\text{V}^{4+}$ -containing, two-dimensional layer, comprised of fluorine bridged corner-sharing and edge-sharing  $\text{VOF}_4(\text{H}_2\text{O})$  octahedral building units. Synthesis was carried out under solvothermal conditions. The  $\text{V}^{4+}$  centre exhibits a typical off-centring, with a short  $\text{V}=\text{O}$  bond and elongated *trans*  $\text{V}-\text{F}$  bond. Hydrogen bonded water molecules occur between the layers. The structure is related to previously reported vanadium oxyfluoride structures, in particular the same layer topology is seen in  $\text{VOF}_3$ .

## 1. Introduction

Our recent work has focused on the preparation of V (IV) oxyfluorides due to their interest as frustrated magnets. We have found that the successful synthesis of two-dimensionally connected vanadium (IV) oxyfluoride structures, for example kagome lattices, requires the use of ionic liquids as solvents (Aidoudi *et al.*, 2011a, 2011b & 2014, Clark *et al.* 2015). On the other hand, there have been several previous reports of solvothermally synthesized vanadium compounds incorporating selenium, which are generally two-dimensional and three-dimensional in nature, and can attribute this high-dimensional structural property to the incorporation of selenium-based anionic linkers (Nguyen *et al.*, 2011 & Glor *et al.*, 2011). Reduced, dimensionally extended vanadium compounds can also be prepared by these routes, for example  $\text{VO}(\text{SeO}_2\text{OH})_2$  (Kim *et al.*, 2010) and  $(4,4'\text{-Bipyridine})\text{V}_2\text{Se}_2\text{O}_8$  (Dai *et al.*, 2003). During solvothermal synthesis experiments, aimed at producing two-dimensional and three-dimensional vanadium (IV) selenites with triangular lattices, a new  $\text{V}^{4+}$  layer structure,  $\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ , (I), was discovered (Fig. 1). This is apparently the first example of a fully reduced  $\text{V}^{4+}$  layered compound synthesized by solvothermal (rather than ionothermal) techniques. The structure is comprised of  $\text{VOF}_4(\text{H}_2\text{O})$  corner and edge-sharing octahedral building units.  $\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ , (I) (or  $\text{VOF}_2(\text{H}_2\text{O}) \cdot 1/2 \text{H}_2\text{O}$ ), is structurally related to previously synthesized vanadium oxyfluoride compounds,  $\text{VOF}_3$  (Supel *et al.*, 2007).

## 2. Experimental

Vanadium trifluoride,  $\text{VF}_3$ , (Alfa, 98%; 0.002 mol, 0.215 g) and ethylene glycol (Fisher 99%+; 0.0032 mol, 0.2 ml) were added to 0.5 ml of a 40% solution of HF (Alfa). Diethylamine\* (Sigma, 99.5%; 0.001 mol, 0.5 ml) and selenious acid (Aldrich 99.999%; 0.001 mol, 0.129 g) were added to the resultant mixture before being sealed in a teflon lined steel autoclave. This was heated at 120 °C for 4 days, then allowed to cool to ambient temperature. The final product was filtered, washed in water and allowed to dry overnight at 60 °C. Crystals were blue blocks, indicating  $\text{V}^{4+}$ , of typical dimension 0.06 x 0.04 x 0.03 mm. These were separated from the bulk product, a brown powder, under an optical microscope. Crystals recovered were too scarce to be analysed using powder X-ray diffraction or to be sent for elemental analysis. \*Guanidine carbonate salt (0.001 mol, 0.09 g) was used in a different experiment in place of diethylamine and produced similar results.

Crystal data, data collection and structure refinement details are summarized in Table 1. Crystals of (I) are monoclinic, in the space group  $C2/c$ . Hydrogen atoms were located from Fourier maps and refined isotropically.

### 3. Results and discussion

The  $\text{VOF}_4(\text{H}_2\text{O})$  building unit of (I) exhibits a single vanadium site in a distorted octahedral environment (Fig. 2), and a single uncoordinated water molecule. The short  $\text{V}=\text{O}$  bond length along with the longer *trans*  $\text{V}-\text{F}$  and *cis*  $\text{V}-\text{OH}_2$  bond lengths are comparable to those seen in the *cis*-building unit of  $[\text{C}_6\text{H}_4\text{N}_{22}][\text{VOF}_4(\text{H}_2\text{O})]_2\cdot\text{H}_2\text{O}$ , (II). (Aldous *et al.*, 2007). Selected bond lengths for (I) and (II) are shown for comparison (Table 2). The octahedral units are linked *via* fluoride ligands to produce a new two-dimensional corner and edge-sharing layer compound of  $\text{V}^{4+}$  (Fig. 3a). Bond valence sum analysis (Brese *et al.*, 1991) confirms the oxidation state of the vanadium centre as  $\text{V}^{4+}$ , oxidized *in situ* from  $\text{V}^{3+}$  (Table 3). The layer in (I) resembles that of the  $\text{VOF}_3$  structure (III) (Supel *et al.*, 2007), with both forming a layer comprised of corner and edge-sharing octahedral units bridged *via* fluoride ligands (Fig. 3 b). Aside the different vanadium oxidation states, there are a number of significant differences between these two structures. The presence of uncoordinated water molecules in (I) results in longer inter-layer  $\text{V}-\text{V}$  distances, due to the H-bonding from O3 to the layer ( $\text{O3}-\text{H2}$ , 1.861 (44) Å and  $\text{H2}-\text{O2}$ , 0.858 (43) Å), compared to those in (III) (Table 4). The elongated *trans* fluoride ligand, F1, in (I) is involved in the edge-sharing  $\text{V}-\text{F}$  bonds, while in (III) the equivalent ligand is involved in the corner-sharing  $\text{V}-\text{F}$  bond. This results in a significant difference in the intra-layer  $\text{V}-\text{V}$  distances (Table 4). The layers of (I) can be seen to stack in a "staggered" manner (Fig. 4a.), while the layers in (III) stack in an "eclipsed" manner (Fig. 4 b.) when both are viewed along [010]. There are many previous examples of layered  $\text{V}^{4+}$  containing compounds that have synthesized solvothermally (Nguyen *et al.* 1995; Massa *et al.*, 2002), however, these compounds owe their two-dimensional structural properties to phosphate and sulfate linkers. More recently there have been examples of  $\text{V}^{4+}$  containing layers, synthesized *via* ionothermal methods (Aidoudi *et al.*, 2011a, 2011b & 2014). These compounds exhibit two-dimensional layers comprised fully of  $\text{V}^{4+}$  corner-sharing octahedral units. This appears to make compound (I) the first example of a purely  $\text{V}^{4+}$  layered compound produced *via* solvothermal techniques. From the presented synthesis route, compound (I) appears as a minor phase, together with a majority unidentified phase(s). Several further attempts to prepare (I) as the majority phase were unsuccessful. The synthetic method will need to be refined in order to produce (I) as the bulk phase, but this could lead to a simpler, more cost-effective route, compared to ionothermal techniques, to obtain layered  $\text{V}^{4+}$  compounds for physical property investigation.

**Table 1**

Experimental details

Crystal data	
Chemical formula	$\text{F}_4\text{H}_6\text{O}_5\text{V}_2$
$M_r$	263.93
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	173
$a, b, c$ (Å)	14.453 (8), 4.8879 (19), 9.663 (5)
$\beta$ (°)	103.24 (2)
$V$ (Å <sup>3</sup> )	664.5 (6)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	2.87
Crystal size (mm)	$0.06 \times 0.04 \times 0.03$
Data collection	
Diffractionmeter	Rigaku SCXmini diffractometer

Absorption correction	Multi-scan REQAB (Rigaku, 1998)
$T_{\min}$ , $T_{\max}$	0.742, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	3138, 750, 585
$R_{\text{int}}$	0.115
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.646
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.035, 0.071, 1.01
No. of reflections	750
No. of parameters	63
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.56, -0.67

Computer programs: *CrystalClear* (Rigaku Corp., 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *Diamond* (Brandenburg, 2009), *WinGX* (Farrugia, 1999).

**Table 2**

Selected bond lengths ( $\text{\AA}$ ) for comparison between (I) and *cis* & *trans*-(II). Relevant bond lengths are also shown for (III).

Compound	Bond	Bond length
(I)	V1=O2	1.592 (2)
	V1—F1	2.174 (2)
	V1—O1	2.027 (3)
<i>cis</i> -(II)	V2=O3	1.641 (3)
	V2—F5	2.084 (3)
	V2—O4	2.035 (3)
<i>trans</i> -(II)	V1=O1	1.606 (3)
	V1—F3	1.960 (2)
	V1—O2	2.305 (3)
(III)	V1=O1	1.551 (2)
	V1—F1	1.972 (2)
	V1—F3	2.294 (2)

**Table 3**

Bond valence parameters.

Atom	$\Sigma s_{(ij)}$
V1	3.942
O2	1.676 <sup>a</sup>
F2	0.514 <sup>b</sup>
F1	0.482 <sup>b</sup>
F2	0.477 <sup>b</sup>
O1	0.517 <sup>a</sup>
F1	0.276 <sup>b</sup>

$s_{(ij)}$  values calculated for  $B = 0.37$ ; (a) Brown & Altermatt (1985). (b) Brese & O'Keeffe (1991).

**Table 4**

Selected V—V distances (Å) for comparison between (I) and (III).

Compound	V—V inter-layer	V—V edge-shared	V—V corner-shared
(I)	5.650 (8)	3.330 (2)	3.704 (5)
(III)	5.070 (6)	3.131 (4)	3.871 (3)

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### Figure 1

Fig. 1. Crystal packing of (I) viewed along the [010] direction.

### Figure 2

Fig. 2. The building unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability. <sup>i</sup> = 1/2 - x, 1/2 - y, 1 - z, <sup>ii</sup> = 1/2 - x, 1/2 + y, 3/2 - z

**Figure 3**

Fig. 3a. The layer of (I) along  $[100]$ . Fig. 3 b. The layer of (III) along  $[100]$ . By comparison with Fig. 3a. the same corner and edge-sharing configuration can be seen, with a terminal *cis*-water and fluoride ligand in (I) and (III) respectively.

**Figure 4**

Fig. 4a. Polyhedral representation of (I), viewed along  $[010]$ , perpendicular to the layers. Fig. 4 b. Polyhedral representation of (III), viewed along  $[010]$ . Note the differences in layer stacking, mediated by the presence of inter-layer water molecules in (I).

# supplementary materials

## V<sub>2</sub>O<sub>2</sub>F<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O: a new V<sup>4+</sup> layer structure related to VOF<sub>3</sub>

### Computing details

Data collection: *CrystalClear* (Rigaku Corp., 2004); cell refinement: *CrystalClear* (Rigaku Corp., 2004); data reduction: *CrystalClear* (Rigaku Corp., 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Diamond* (Brandenburg, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

### (I)

#### Crystal data

F<sub>4</sub>H<sub>6</sub>O<sub>5</sub>V<sub>2</sub>  
*M<sub>r</sub>* = 263.93  
 Monoclinic, C2/c  
 Hall symbol: -C2yc  
*a* = 14.453 (8) Å  
*b* = 4.8879 (19) Å  
*c* = 9.663 (5) Å  
 $\beta$  = 103.24 (2)°  
*V* = 664.5 (6) Å<sup>3</sup>  
*Z* = 4

*F*(000) = 512  
*D<sub>x</sub>* = 2.638 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 1673 reflections  
 $\theta$  = 3.5–28.9°  
 $\mu$  = 2.87 mm<sup>-1</sup>  
*T* = 173 K  
 Block, blue  
 0.06 × 0.04 × 0.03 mm

#### Data collection

Rigaku SCXmini  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 dtprofit.ref scans  
 Absorption correction: multi-scan  
 REQAB (Rigaku, 1998)  
*T<sub>min</sub>* = 0.742, *T<sub>max</sub>* = 1.000  
 3138 measured reflections

750 independent reflections  
 585 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.115  
 $\theta_{\max}$  = 27.3°,  $\theta_{\min}$  = 2.9°  
*h* = -18→18  
*k* = -6→6  
*l* = -12→12  
 1080 standard reflections every 1 reflections

#### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.035  
*wR*(*F*<sup>2</sup>) = 0.071  
*S* = 1.01  
 750 reflections  
 63 parameters  
 0 restraints  
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring sites  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0095P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max}$  = 0.030  
 $\Delta\rho_{\max}$  = 0.56 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.67 e Å<sup>-3</sup>

# Special details

## Refinement

Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

## Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
V1	0.18501 (4)	0.19656 (10)	0.61917 (6)	0.00822 (18)
F1	0.19765 (13)	0.4512 (4)	0.4665 (2)	0.0113 (4)
F2	0.21071 (14)	−0.1169 (4)	0.7467 (2)	0.0125 (4)
O1	0.10702 (19)	−0.0680 (5)	0.4776 (3)	0.0133 (6)
O2	0.09784 (17)	0.3392 (4)	0.6657 (3)	0.0136 (5)
O3	0.0000	0.1972 (8)	0.2500	0.0137 (8)
H1	0.127 (3)	−0.201 (9)	0.467 (5)	0.027 (14)*
H2	0.070 (3)	−0.001 (10)	0.403 (5)	0.036 (14)*
H3	0.033 (3)	0.292 (8)	0.230 (6)	0.037 (16)*

## Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
V1	0.0096 (3)	0.0066 (3)	0.0085 (3)	0.0004 (2)	0.0022 (2)	0.0001 (2)
F1	0.0159 (11)	0.0086 (9)	0.0100 (10)	0.0018 (7)	0.0042 (9)	0.0012 (8)
F2	0.0149 (10)	0.0092 (9)	0.0119 (12)	0.0009 (7)	0.0004 (9)	0.0039 (8)
O1	0.0166 (14)	0.0084 (13)	0.0132 (15)	0.0010 (11)	0.0001 (11)	−0.0019 (12)
O2	0.0137 (11)	0.0114 (12)	0.0157 (15)	0.0022 (9)	0.0035 (11)	−0.0009 (10)
O3	0.0150 (18)	0.0108 (17)	0.015 (2)	0.000	0.0032 (16)	0.000

## Geometric parameters ( $\text{\AA}$ , $^\circ$ )

V1—O2	1.592 (2)	V1—O1	2.027 (3)
V1—F2	1.948 (2)	V1—F1 <sup>ii</sup>	2.174 (2)
V1—F1	1.971 (2)	F1—V1 <sup>ii</sup>	2.174 (2)
V1—F2 <sup>i</sup>	1.972 (2)	F2—V1 <sup>iii</sup>	1.972 (2)
O2—V1—F2	102.39 (11)	F2 <sup>i</sup> —V1—O1	164.14 (10)
O2—V1—F1	98.60 (11)	O2—V1—F1 <sup>ii</sup>	171.78 (11)
F2—V1—F1	159.00 (9)	F2—V1—F1 <sup>ii</sup>	85.83 (8)
O2—V1—F2 <sup>i</sup>	98.46 (11)	F1—V1—F1 <sup>ii</sup>	73.18 (8)
F2—V1—F2 <sup>i</sup>	86.65 (5)	F2 <sup>i</sup> —V1—F1 <sup>ii</sup>	81.86 (9)
F1—V1—F2 <sup>i</sup>	90.68 (9)	O1—V1—F1 <sup>ii</sup>	83.84 (10)
O2—V1—O1	96.67 (13)	V1—F1—V1 <sup>ii</sup>	106.82 (8)
F2—V1—O1	85.48 (11)	V1—F2—V1 <sup>iii</sup>	141.81 (11)
F1—V1—O1	91.75 (11)		

Symmetry codes: (i)  $-x+1/2, y+1/2, -z+3/2$ ; (ii)  $-x+1/2, -y+1/2, -z+1$ ; (iii)  $-x+1/2, y-1/2, -z+3/2$ .